DoD Environmental Monitoring & Data Quality Workshop

EMDQ 2011

March 28 – April 1, 2011 • Arlington, VA

Using Stable Isotope Ratio Analysis to Distinguish Perchlorate Sources

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Perchlorate Contamination in the United States: Historical

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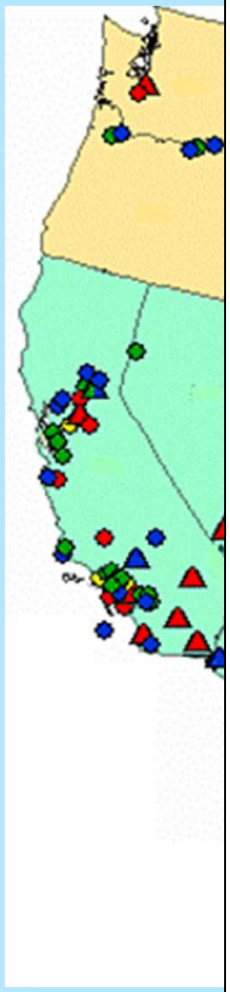
Military and Aerospace Issue

Limited Sources

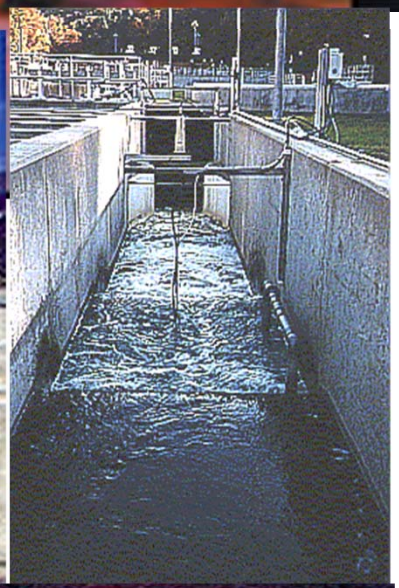
- Rocket Testing
- Hog-Out
- Manufacturing
- Training Areas
- OB/OD Areas
- Few Commercial Sites

Perchlorate Detections In Food (US FDA)



Map sou

Food Group	Number of Samples	Average Residue (ppb)
Lettuce	137	10.3
Milk	125	5.81
Tomatoes	73	13.7
Spinach	36	115
Greens	14	92.4
Cabbage	13	8.80
Cantaloupes	48	28.6
Carrots	59	15.8
Green Beans	19	6.12
Broccoli	14	8.49
Grapes	12	8.58



Other (Non-Military) Sources??

A. Natural Perchlorate

1. Chilean Caliche – Atacama Desert - natural nitrogen fertilizer
2. Mineral deposits – Death Valley, CA
3. Southwest soils and groundwater

B. Other Anthropogenic

1. Fireworks
2. Road Flares
3. Perchloric Acid and Reagents
4. Chlorate (herbicide)
5. Chlorine Bleach

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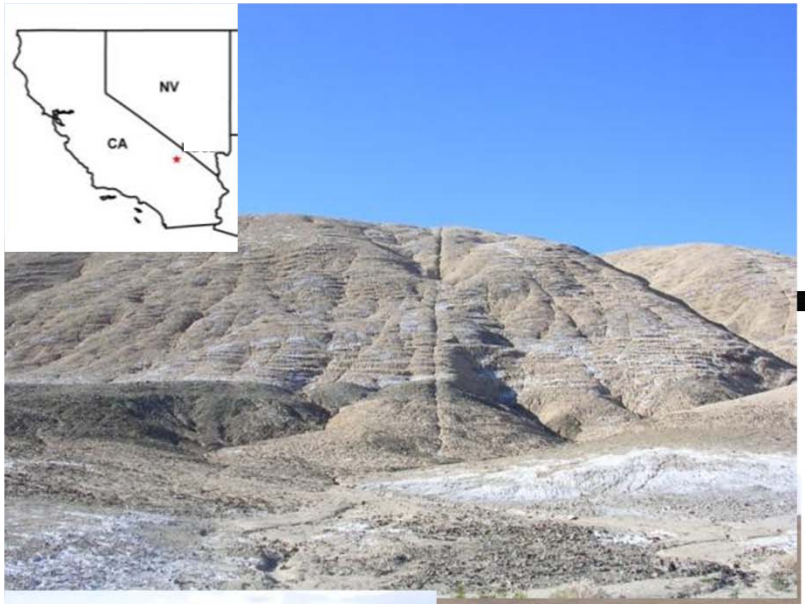
Chilean Nitrate

- **Uses**
  - Critical N fertilizer during 19th & early 20th C (cotton, tobacco and citrus)
  - Explosives manufacture
- **Perchlorate Source**
  - 1910-1960
    - US imported 10^9kg fertilizer /year
    - 0.2% ClO_4^- (highly variable)
    - 10^6kg ClO_4^- /year
- **Historical Impact**
  - Citrus or cotton ~50 mg/m^2-year
  - Possible large local Impacts

** Dasgupta, PK, et al. 2006. Perchlorate in the United States. Analysis of Relative source contributions to the Food Chain. Environ. Sci. Technol. 40;6608-6614*



Natural Perchlorate in the USA

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- **Indigenous Perchlorate**
  - * *Natural nitrate deposits*
  - * *Perchlorate in soils*
  - * *Perchlorate in groundwater & rainwater*
    - *Atmospheric formation with O_3*
    - *Other mechanisms – UV, TiO_2*

Death Valley Nitrate Deposits

		concentration			
site	nonsoluble fraction	ClO_4^-	Cl^-	NO_3^--N	SO_4^{-2}
Death Valley	%	mg kg^{-1}		g kg^{-1}	
Confidence Hills 1	NA	0.25	320	1.8	72
Confidence Hills 2	49	0.85	180	5.5	100
Saratoga Hills	78	0.95	63	5.9	23
Bully Hill	62	0.82	80	28	6.5
Zabriskie	64	1.7	140	4.4	39
Atacama					
P1	42	243	80	12	57
P2	50	328	456	44	84
P3	13	113	50	15	51
P4	51	132	61	22	51

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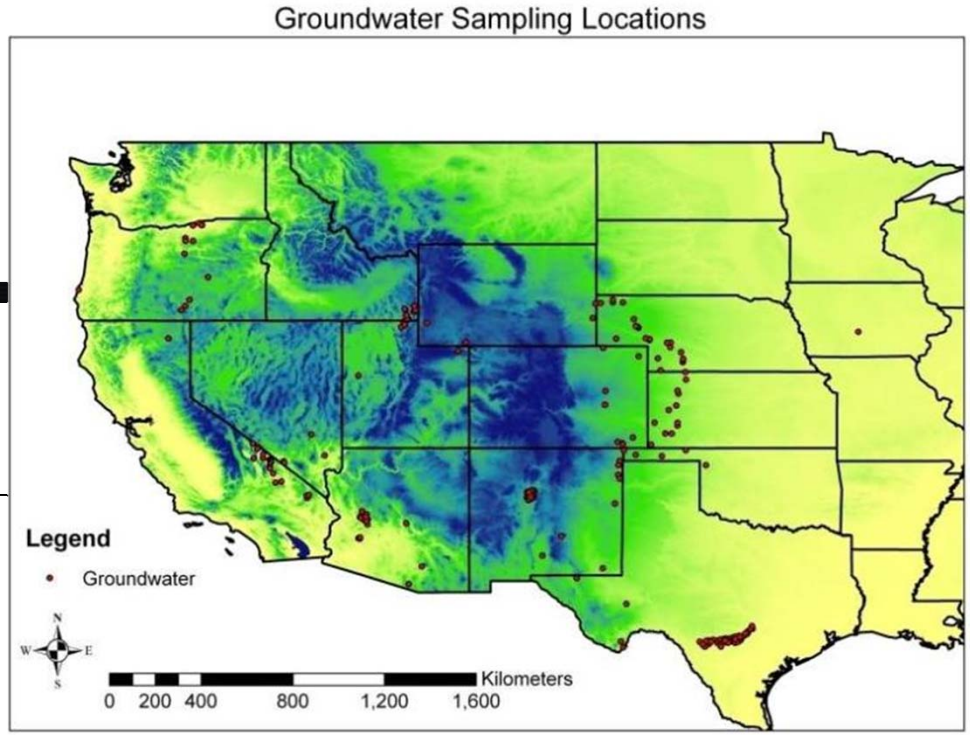
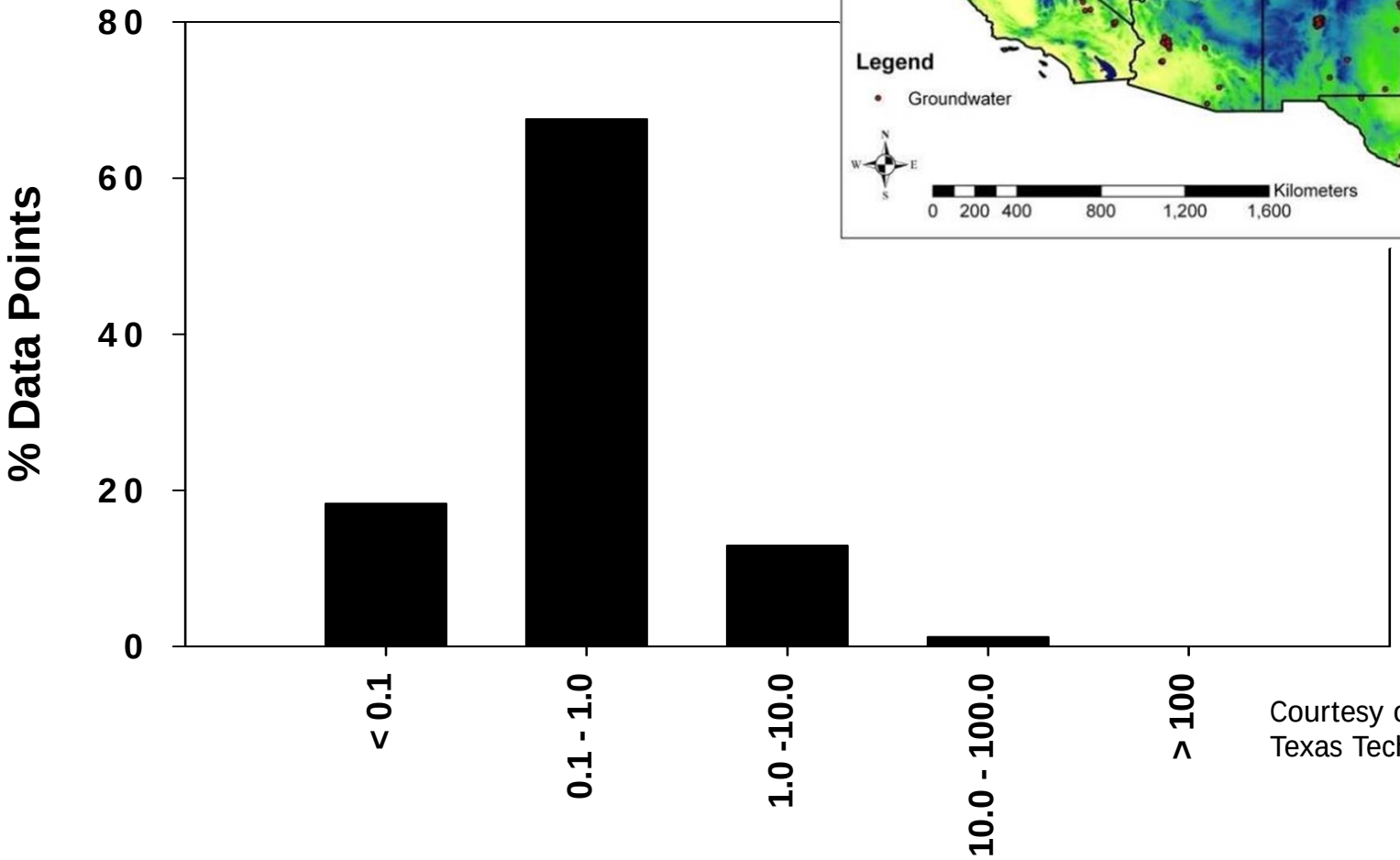
Concentrations in in Western US Groundwater





Courtesy of Dr. W. Andrew Jackson, Texas Tech

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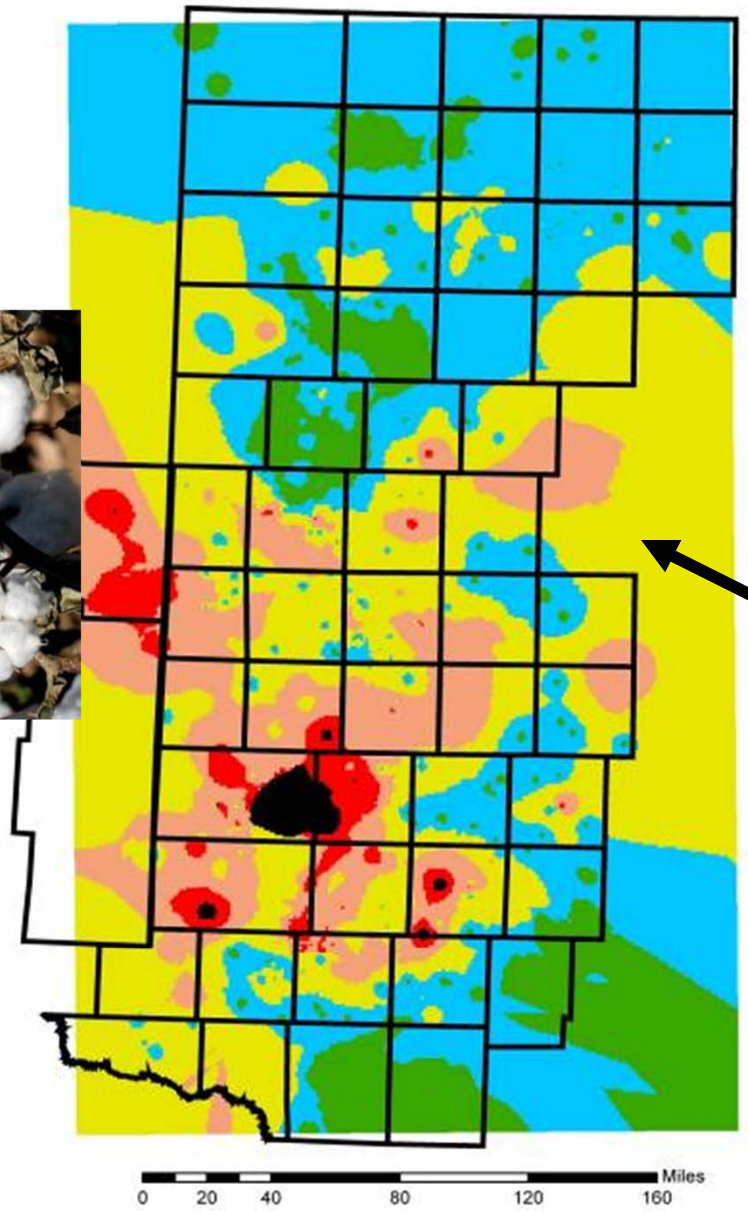
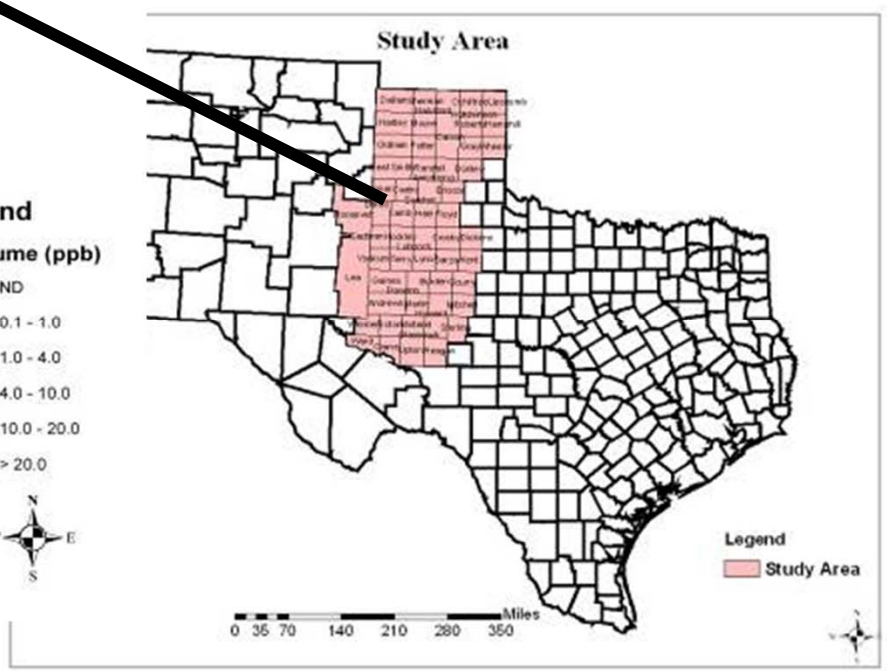
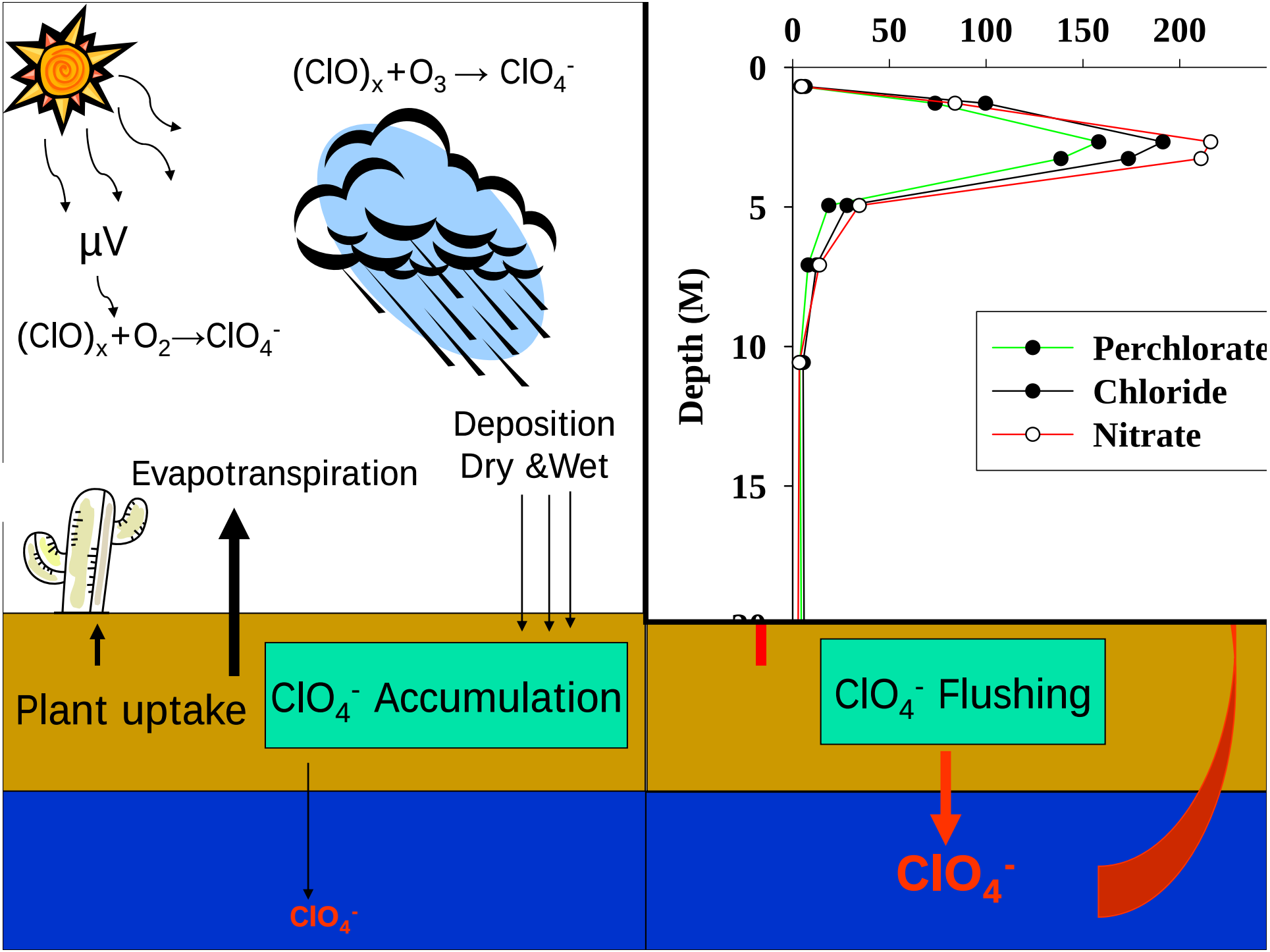
West Texas – Southern High Plains

- Study area >59,000 mi^2
- 89% > 0.1 ppb
- Estimated Mass of ClO_4^-
  - Saturated >2 X 10^6 Kg






$(ClO)_x + O_3 \rightarrow ClO_4^-$
μV
$(ClO)_x + O_2 \rightarrow ClO_4^-$
Deposition
Dry &Wet
Evapotranspiration
Plant uptake
ClO_4^- Accumulation
ClO_4^-
ClO_4^- Flushing
ClO_4^-
0
50
100
150
200
0
5
10
15
Depth (M)
Perchlorate
Chloride
Nitrate

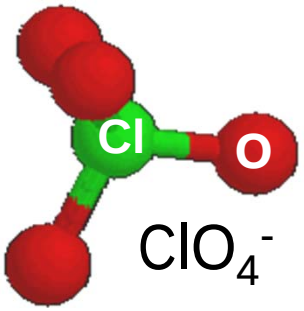
Can You Distinguish Natural from Synthetic Perchlorate?

Stable Isotope Ratio Analysis of Chlorine and Oxygen in Perchlorate

- **Other Lines of Evidence**
  - ^{36}Cl Analysis
  - Groundwater Dating
  - Co-Contaminants
  - Other Geochemical Data

Stable Isotope Ratio Analysis: Perchlorate

- Methods developed for analysis of both chlorine and oxygen isotopes in perchlorate. Dual isotope comparisons possible.
- Analyzed by IRMS with a precision of about ± 0.1 to 0.4‰
- Sample preparation is critical. Methods have been developed to collect, recover, and purify perchlorate.



Elements in a compound can have widely different isotopic ratios based on mode of formation (e.g.,^{18}O in NO_3 from nitrification vs. atmospheric). Stable isotope ratios can provide a unique "fingerprint"

Hydrogen	^{1}H, ^{2}H
Oxygen	^{16}O, ^{17}O, ^{18}O
Carbon	^{12}C, ^{13}C
Chlorine	^{35}Cl, ^{37}Cl
Nitrogen	^{14}N, ^{15}N
Sulfur	^{32}S, ^{34}S

Stable Isotope Analysis: Perchlorate

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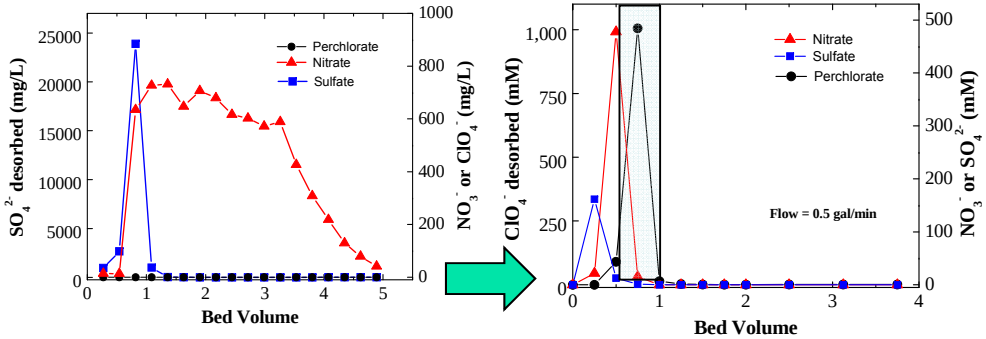
ESTCP

Sample Collection (5-10 mg)

ClO_4^- on IX resin (NO_3^-, SO_4^{2-}, ReO_4)

Preserved with HCl and 4ºC

Sample Extraction & Purification

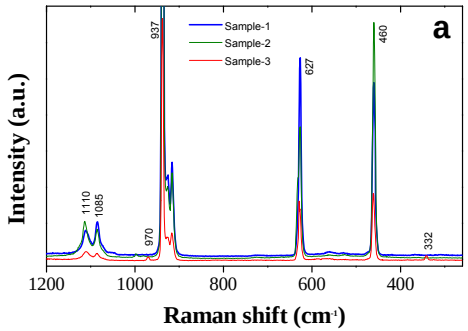


Leach with 4M HCl to remove NO_3^- & SO_4^{2-}, CO_3- & some humics

Leach with 1M $FeCl_3$ + 4MHCl ($FeCl_4$) -collect fractions

* Neutralize -Remove FeO_3
* Concentrate ClO_4 supernatant
* Filter unwanted precipitates
* Crystallize ClO_4 as $CsClO_4$ or KCO_4
* Wash crystals with MeOH

Verification of Purity



Crystal morphology
Ion chromatography(lg sample)
Micro-Raman spectroscopy

Impurity detected

IRMS – $\delta^{37}Cl$

Cl^-

Weigh crystal
Combust to Cl salt
Convert to CH_3Cl
Purify via GC
IRMS
Determine Cl isotope ratio

IRMS – $\delta^{18}O/\delta^{17}O$

Weigh crystal
$\delta^{18}O$: Combust to CO
($\delta^{18}O$ & $\Delta^{17}O$): decompose to O_2
IRMS (CO & O_2)
Measure yields
Determine O isotope ratios

Terminology:
Stable Isotope Ratio Analysis

Terminology:

*Isotopic compositions of light elements are generally reported as "delta" (δ) values in parts-per-thousand (denoted "‰" = per mil) deviations (enrichments or depletions) relative to a known standard

Equation 1. δ **(in ‰) =** $(R_x/R_s - 1) * 1000$

R = ratio heavy/light isotope (e.g., $^{37}Cl/^{35}Cl$**)**

Rx = sample (e.g., $^{37}Cl/^{35}Cl$ **in environmental sample)**

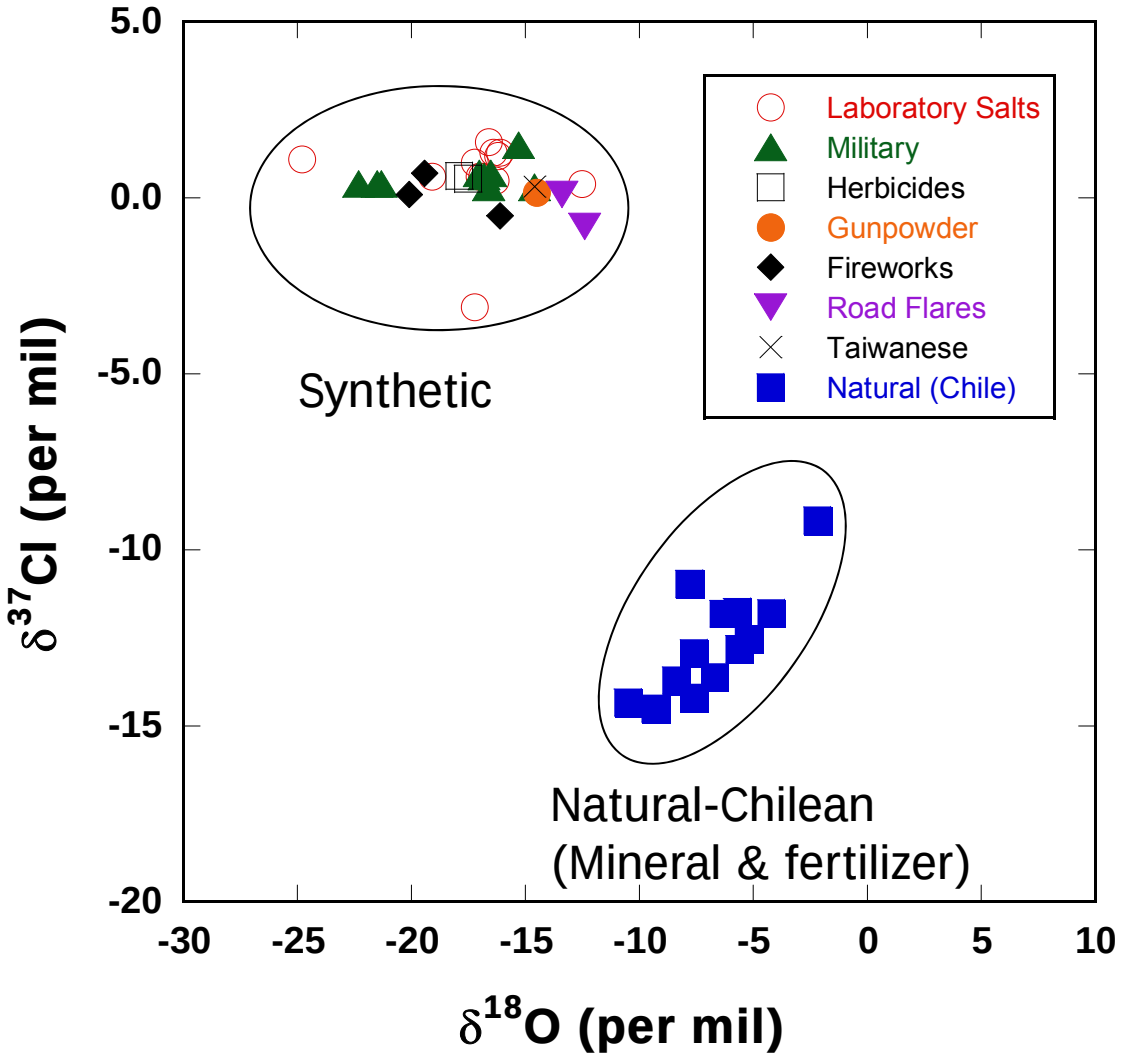
Rs = standard (e.g., $^{37}Cl/^{35}Cl$ **in chlorine standard "SMOC")**

*** Example:** $\delta^{37}Cl = +30$ ‰

30 parts-per-thousand (3 %) more ^{37}Cl **in sample relative to a known standard (Standard Mean Ocean Chloride; SMOC).**

(^{18}O **= SMOW)**

Forensic Isotopic Analysis: Chilean vs. Synthetic $\delta^{37}Cl$ and $\delta^{18}O$



Chlorine markedly "heavier" in synthetic perchlorate (n = 43).

$\delta^{37}Cl$: **0.5 ± 1.0**

$\delta^{18}O$: **-17.5 ± 2.7**

Oxygen consistently "heavier" in natural (Chilean) perchlorate (n = 13).

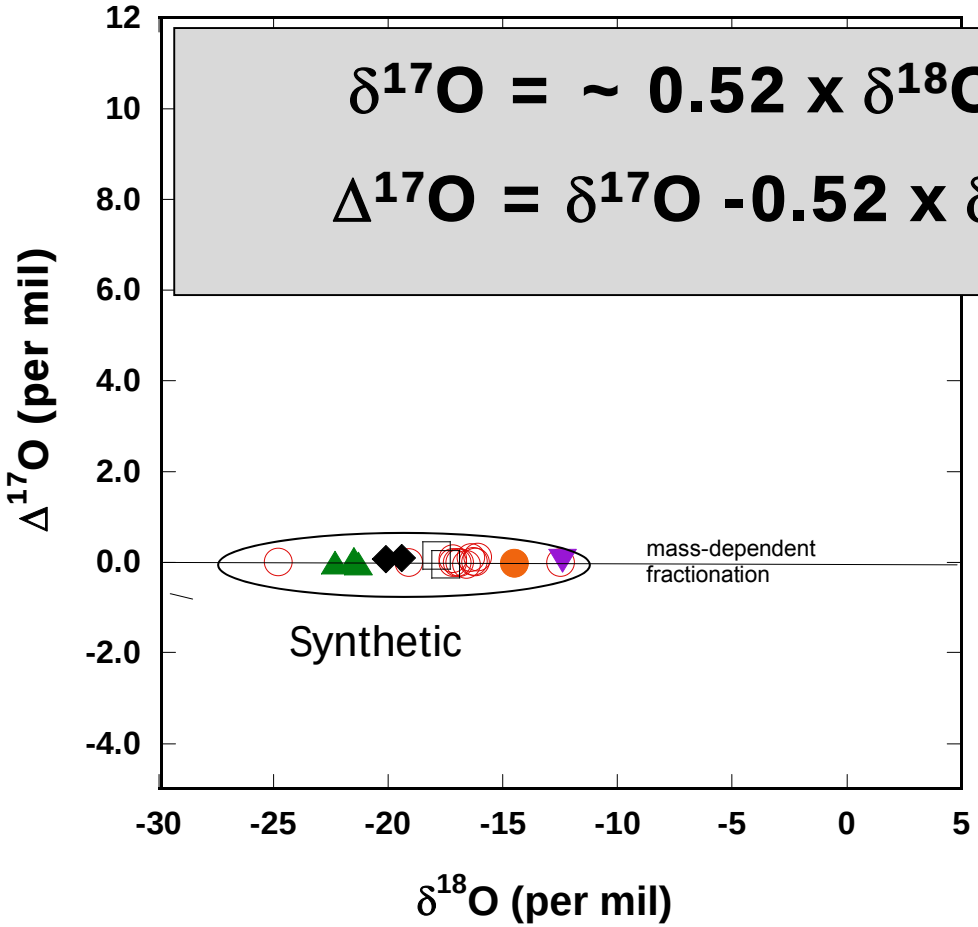
$\delta^{37}Cl$: **-12.6 ± 1.5**

$\delta^{18}O$: **-6.7 ± 2.2**

Forensic Isotopic Analysis: Chilean vs. Synthetic $\Delta^{17}O$ and $\delta^{18}O$

$\delta^{17}O = \sim 0.52 \times \delta^{18}O$

$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O \quad (= O)$



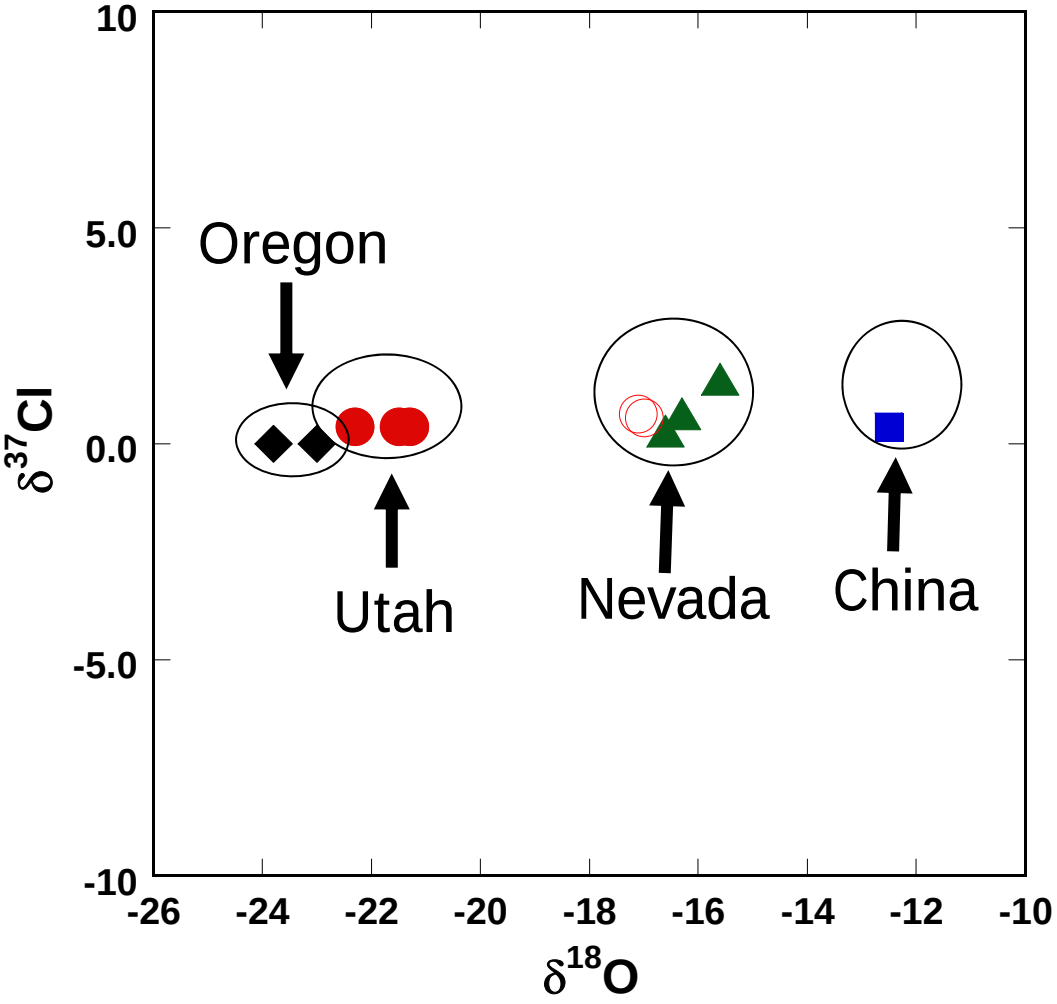
Synthetic perchlorate "mass dependent" fractionation (n = 43)

$\Delta^{17}O$: 0.01 ± 0.06

Range: - 0.24 to 0.11

Bohlke, J.K., N.C. Sturchio, B. Gu, G.M. Brown, J. Horita, W. A. Jackson, J. Batista, and P. B. Hatzinger. 2005. Perchlorate isotope forensics. Analytical Chemistry, 77; 7838-7842.

Can You Differentiate Synthetic Sources?

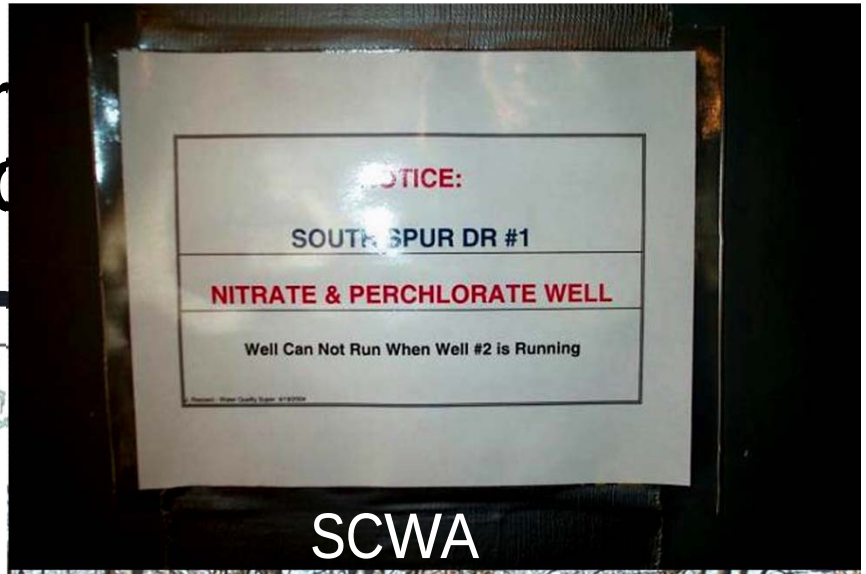


1. **There are some isotopic differences between manufacturers – but only in ^{18}O.**

2. **H_2O is the source of oxygen in synthetic perchlorate and ^{18}O in H_2O varies globally.**

3. **Small dataset**
   - batch to batch variation?
   - variation with time?
   - different “sources” in products (e.g., flares)?


Depot Lane

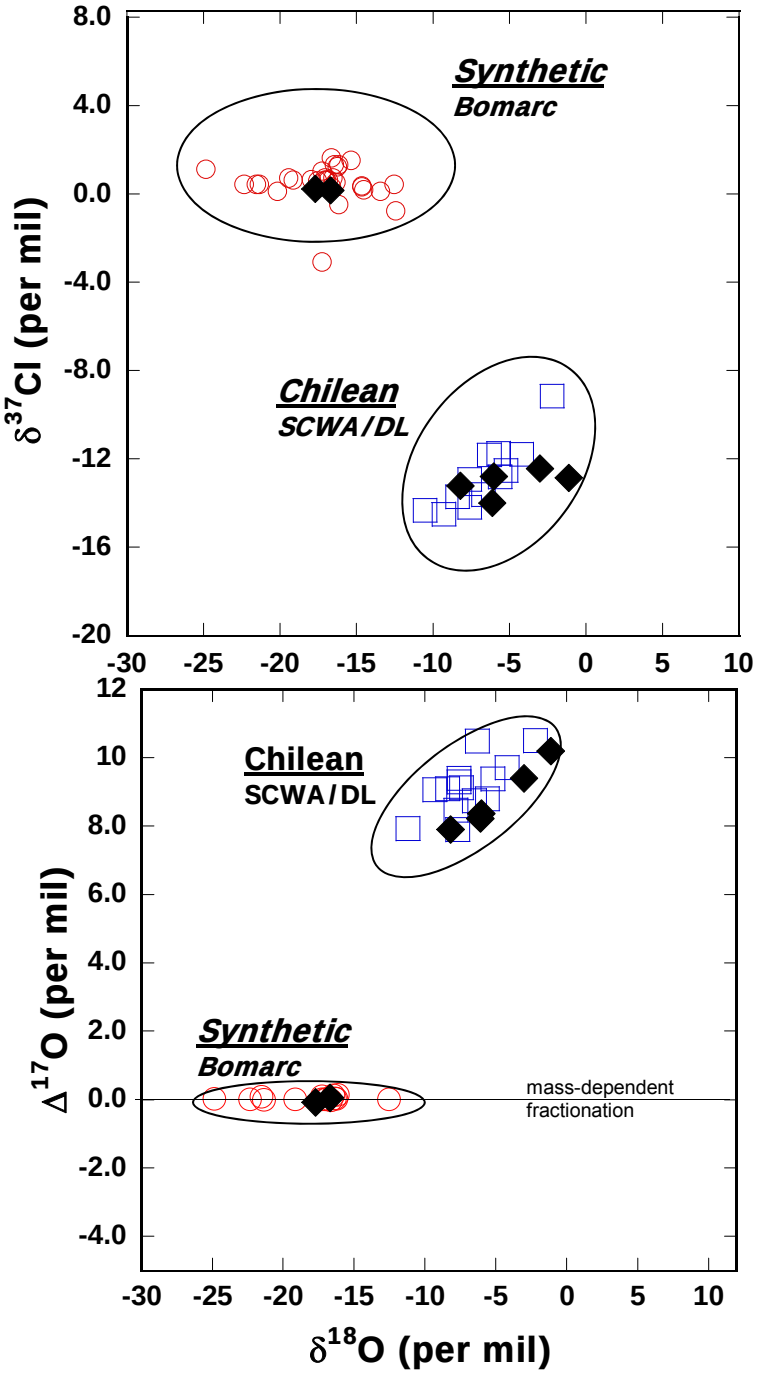

TICE:
SOUTH SPUR DR #1
NITRATE & PERCHLORATE WELL
Well Can Not Run When Well #2 is Running

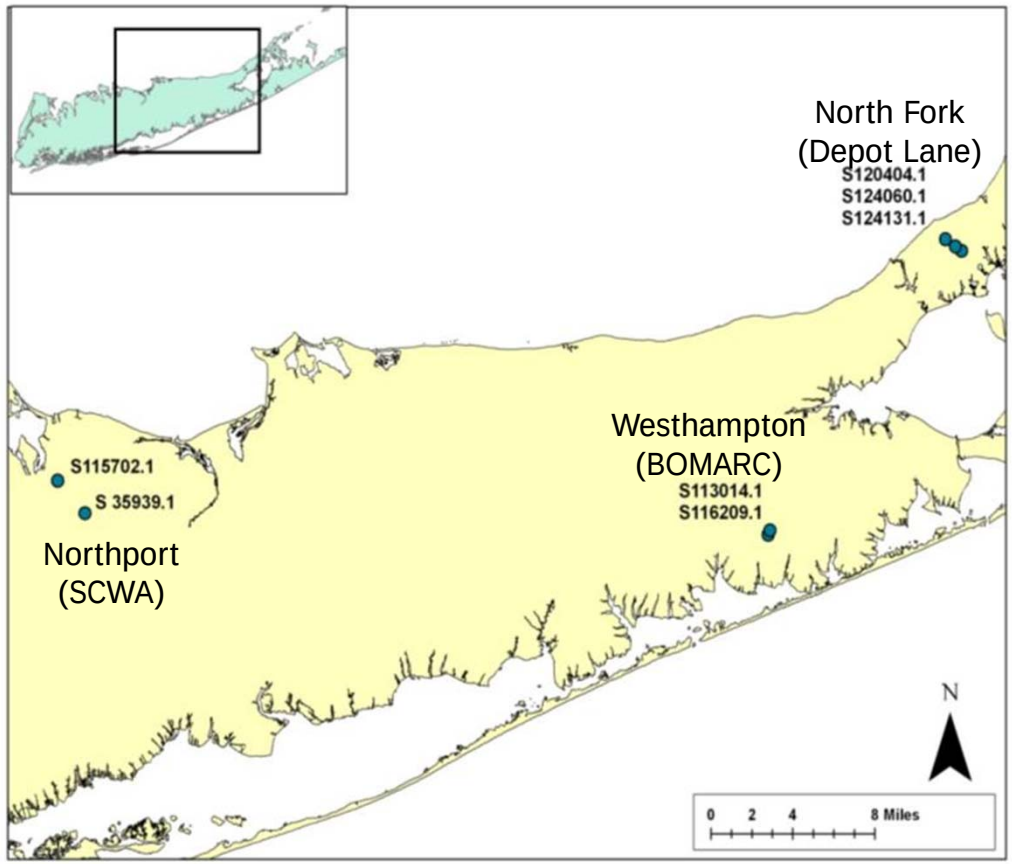
SCWA


BOMARC

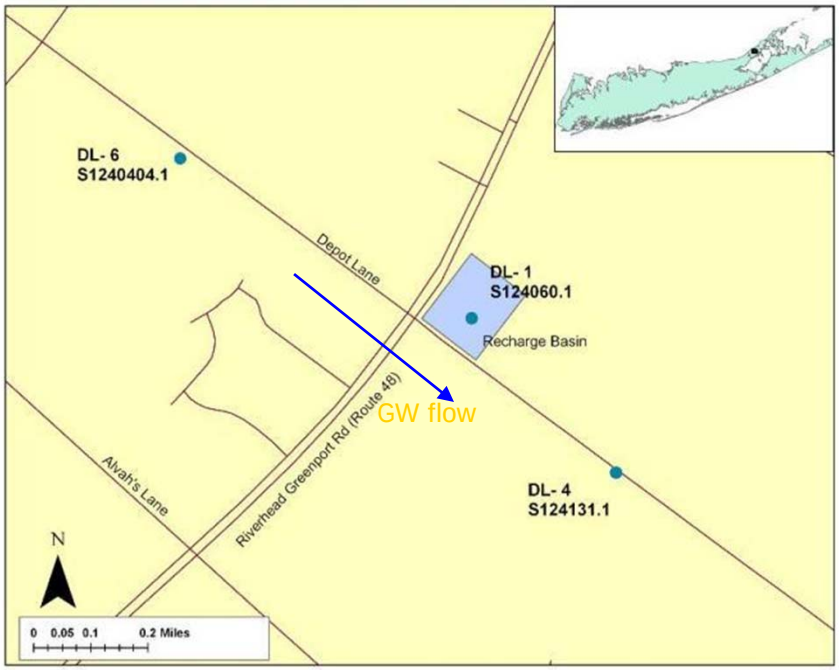

4

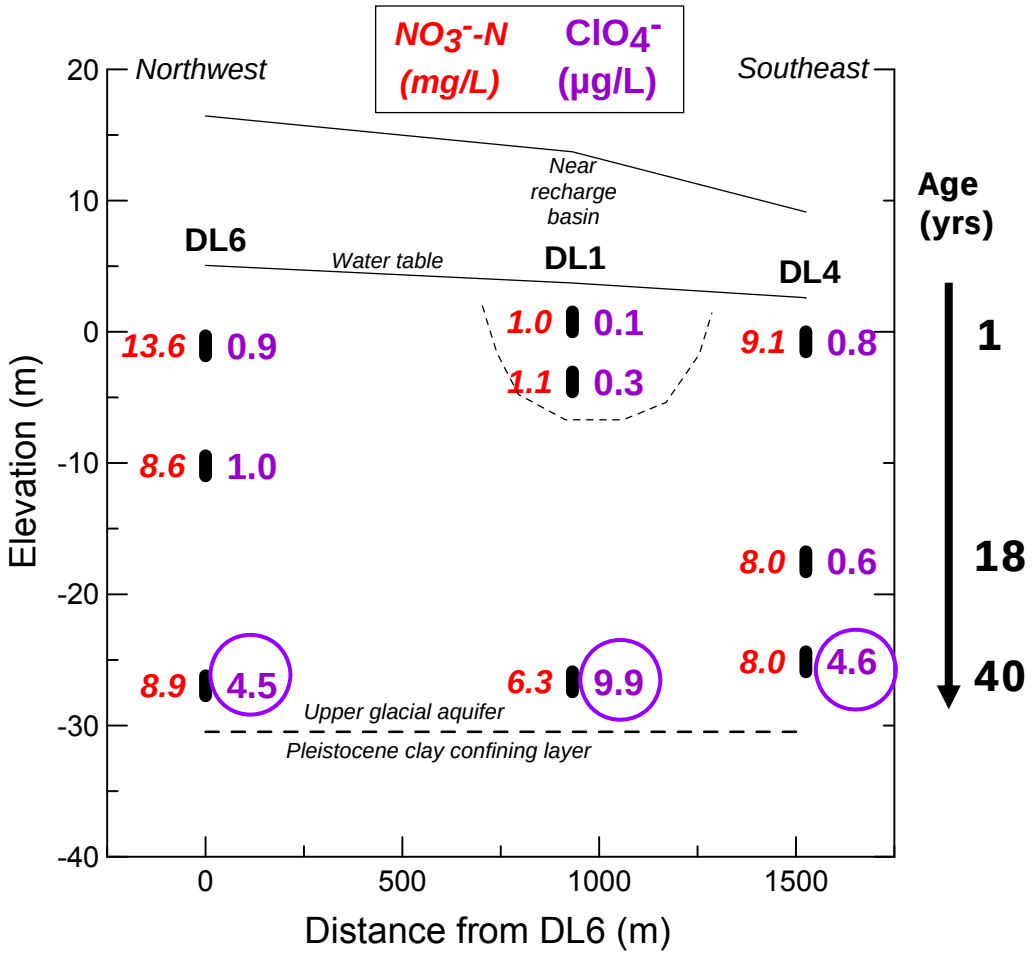
Case Study: Long Island, NY





Long Island, NY
Depot Lane Transect





Isotope Results: Groundwater Data from Various Sites Compared to Chilean and Synthetic Sources

Anthropogenic

Long Island, NY
Amherst, MA
Edwards AFB, CA
Henderson, NV
Southern California (2)
Elkton, MD
Dahlgren, VA
Israel

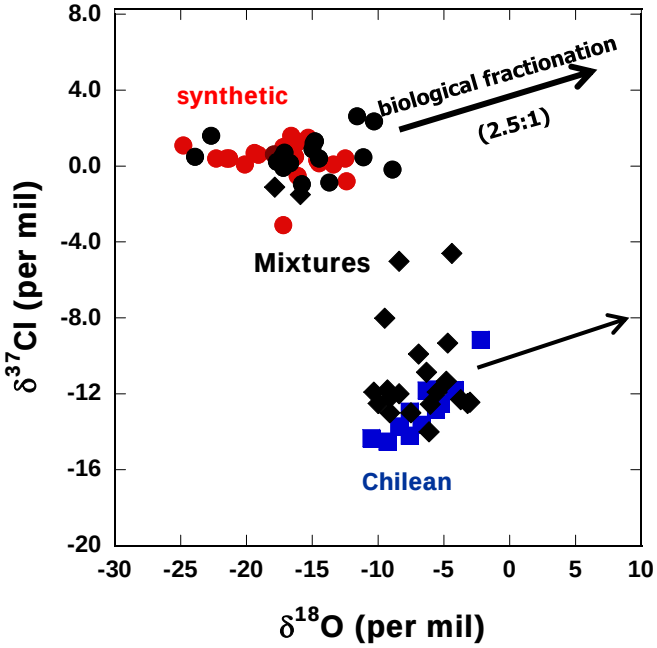
Chilean Fertilizer

Long Island
Southern California (3)
New Jersey

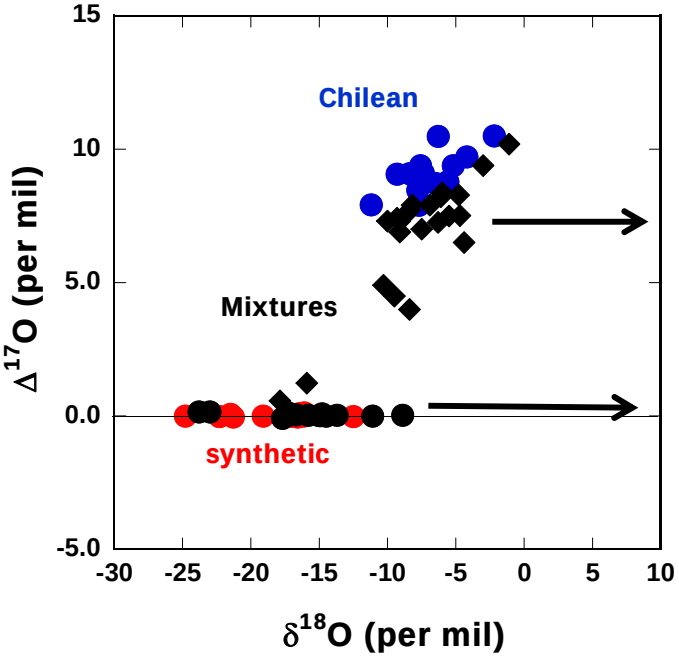
Mixtures:

Southern California (2)

Comparison of $\delta^{37}Cl$ and $\delta^{18}O$ of perchlorate in groundwater from to synthetic solids and natural Chilean sources



Comparison of $\delta^{18}O$ and $\Delta^{17}O$ of perchlorate in groundwater to various synthetic solids and natural Chilean sources



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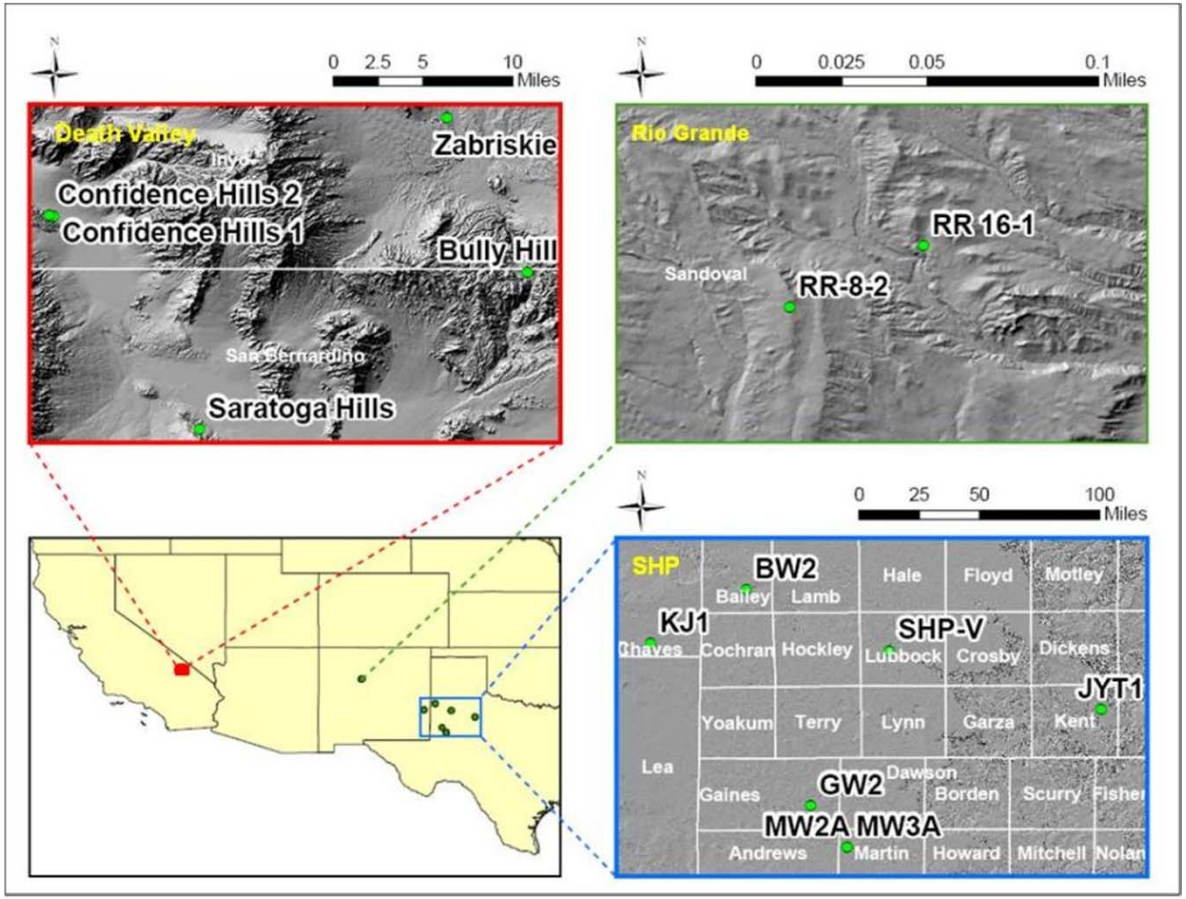
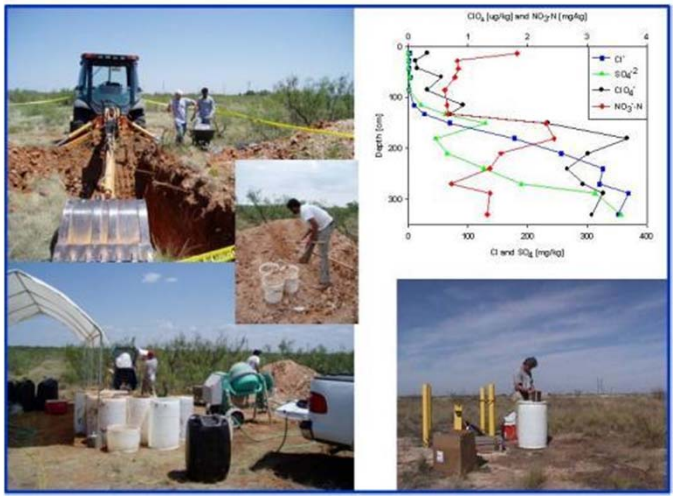
Indigenous Natural Perchlorate

Death Valley Caliche



Rio Grande Basin Groundwater (Ancient)



SHP Groundwater and Vadose Soil

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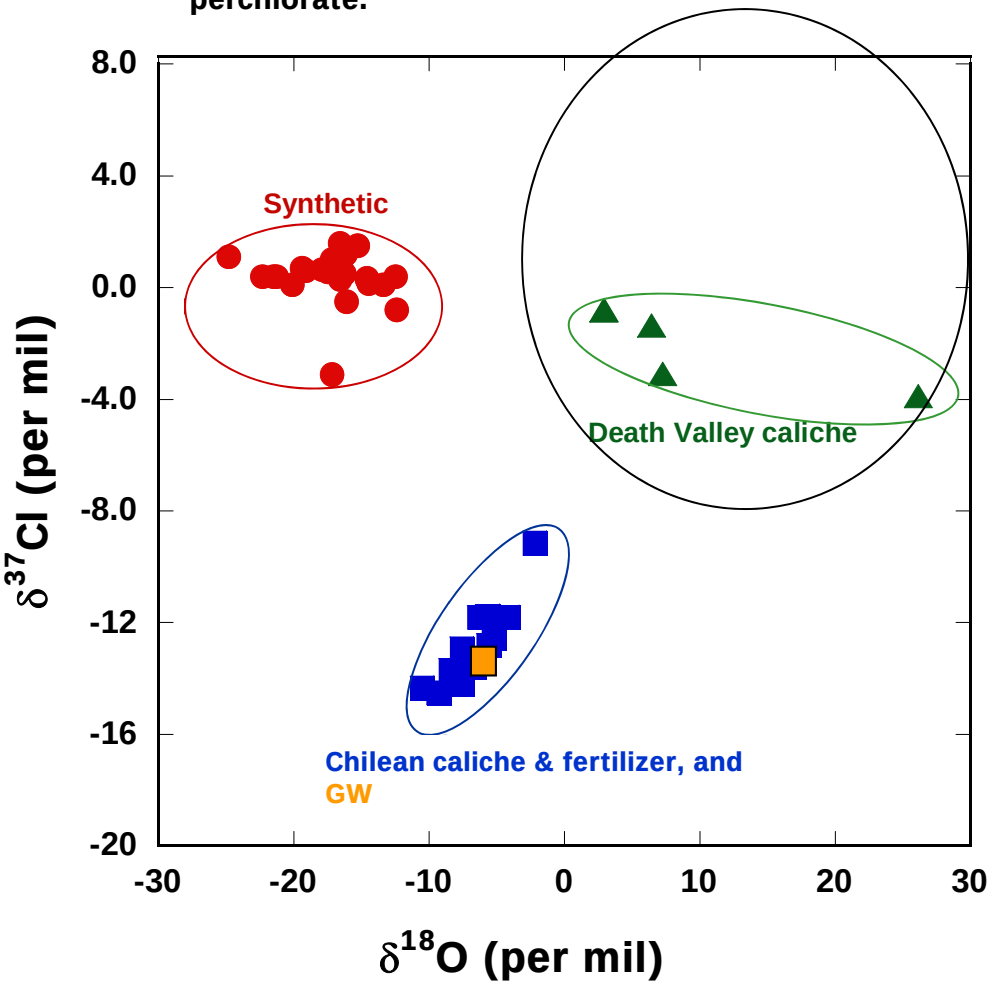
Indigenous Perchlorate: $\delta^{37}Cl$ and $\delta^{18}O$

Comparison of $\delta^{37}Cl$ and $\delta^{18}O$ in perchlorate from indigenous US sources with Chilean and synthetic perchlorate.



1. **There are multiple signatures for natural perchlorate but all are readily distinguished from synthetic sources via ^{37}Cl and ^{18}O.**
2. **West Texas vadose (soil) perchlorate has a similar isotope signature to that in West Texas & NM groundwater.**

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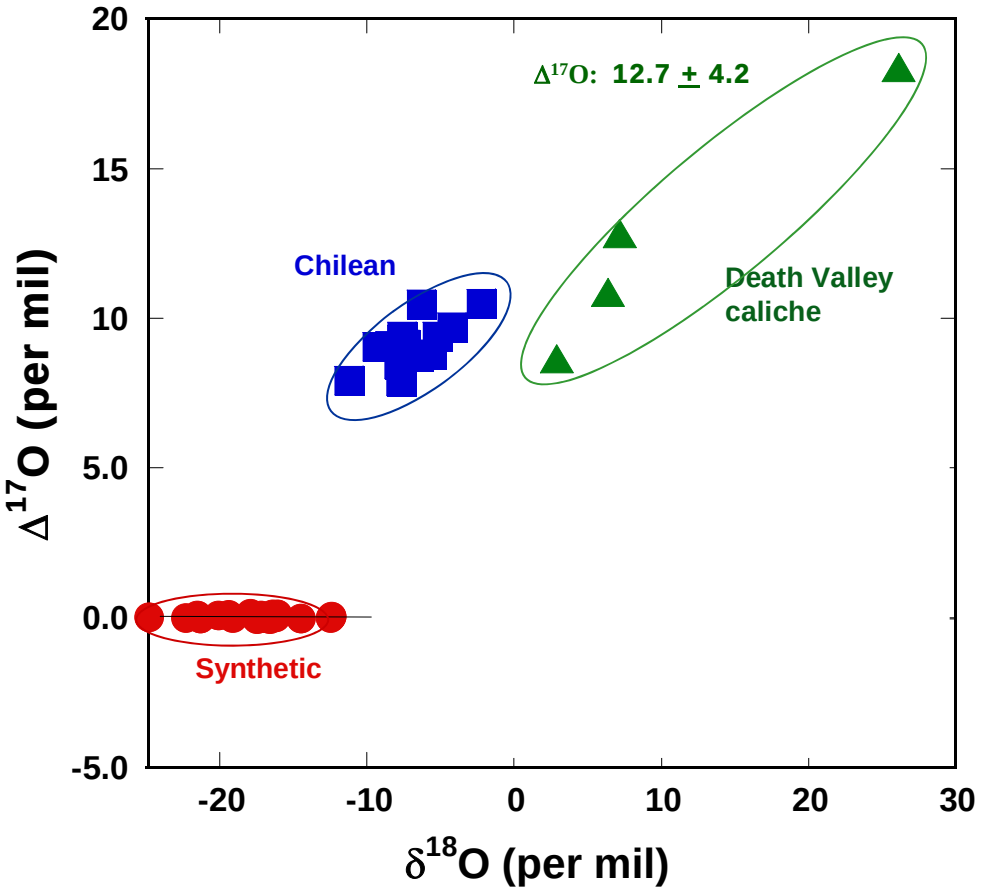
Indigenous Perchlorate: $\Delta^{17}O$ and $\delta^{18}O$

Comparison of $\Delta^{17}O$ and $\delta^{18}O$ in perchlorate from indigenous US sources with Chilean and synthetic perchlorate.



1. Like Chilean samples, Death Valley deposits have significant excess ^{17}O in perchlorate.

2. SHP soil and groundwater has only slight $\delta^{17}O$ excess – no difference between saturated and unsaturated zone??

3. Understanding the origin of natural perchlorate (and the resulting isotope values) is currently the subject of significant research.

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Perchlorate Origin - Wh

Understanding of Natural Perchlorate Origin:

Why is $\Delta^{17}O$ so low in SHP Perchlorate ?

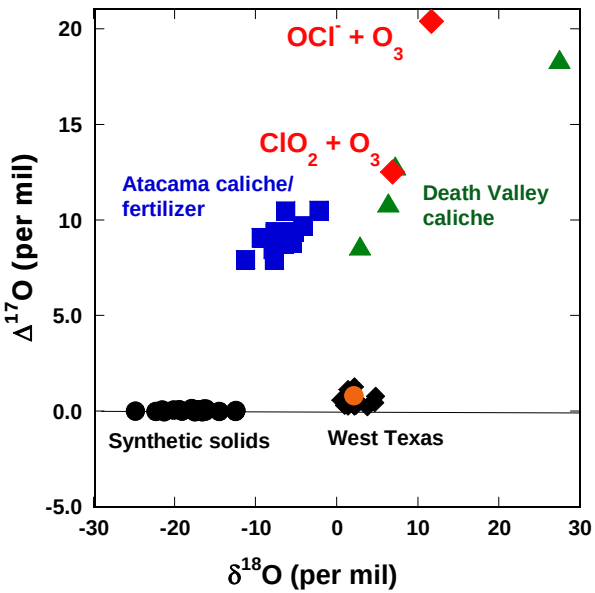
(1) *Different reaction mechanism and/or location.*

- ***Ozone vs. UV reaction?***
- ***Atmosphere vs. surface catalyzed?***
- ***What does ^{36}Cl tell us?***

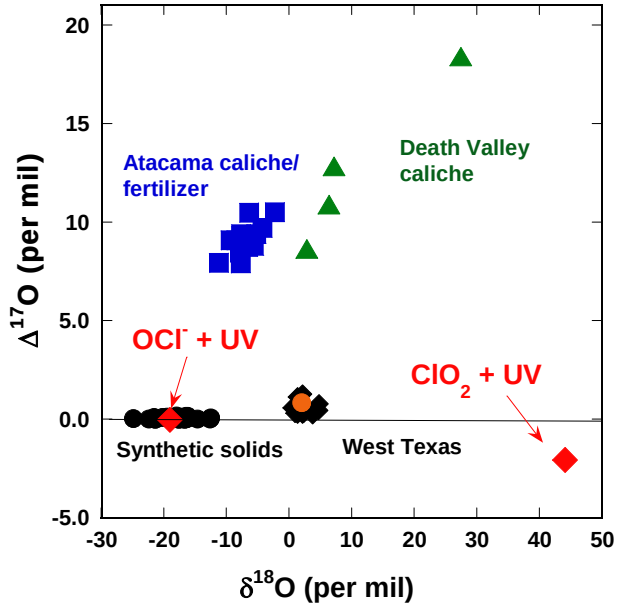
(2) *Post-depositional modification.*

- ***Does oxygen in perchlorate exchange with water?***
- ***Role of plants or microorganisms?***

Perchlorate generated with O_3



Perchlorate generated with UV



^{36}Cl Analysis

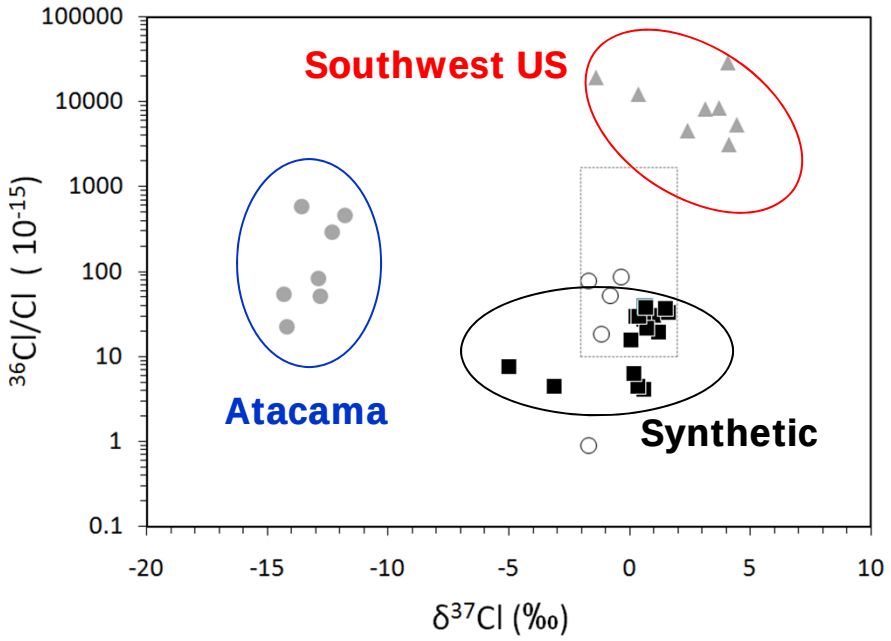
^{35}Cl	^{36}Cl	^{37}Cl
34.96885	t½=301,000 yrs	36.96590
75.77%		24.23%
Stable	Cosmogenic/ anthropogenic	Stable

Long-lived radioisotope produced in the stratosphere from ^{40}Ar ($T^{1/2}$ = ~ 301,000 yrs)

$^{36}Cl/Cl$ = ~ 700 x 10^{-15}

Analyzed by *Accelerator Mass Spectrometry (AMS)*

Analyzed purified perchlorate samples
- Southwest US
- Atacama
- Synthetic



1. **Southwest perchlorate (SHP and DV) significantly enriched in ^{36}Cl – Irrespective of δ^{17}O.**

2. **Suggests significant component of "young" atmospheric perchlorate.**

3. **Atacama most likely "old" atmospheric perchlorate**

Sturchio N.C., Caffee M.R., Beloso A. D., Heraty L.J., Böhlke J.K., Gu B., Jackson W.A., Hatzinger P.B., Heikoop J.R., and Dale M., 2009. Chlorine-36 as a tracer of perchlorate origin. Environmental Science & Technology 43, 6934–6938.

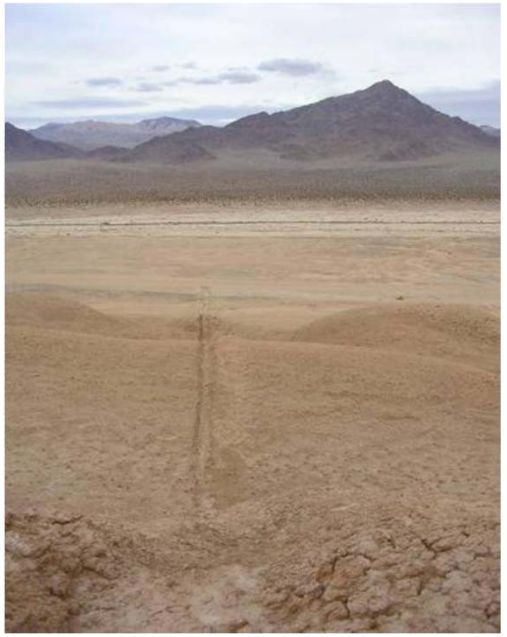
Perchlorate Forensic Analysis: Summary

- When perchlorate is detected at low concentrations (< 10 μg/L) in groundwater, natural sources should be considered.

- Isotope analyses ($\delta^{37}Cl$, $\delta^{18}O$, $\delta^{17}O$ and $^{36}Cl/Cl$) can be used to distinguish between synthetic and natural sources – Four independent measurements.

- Natural perchlorate (from Chilean fertilizer and from "indigenous" sources) has been detected in numerous wells in the US via isotope analysis.

- A "Guidance Manual" for perchlorate isotope sampling is presently under development by SERDP/ESTCP.



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